SOP for the DETERMINATION OF HALOACETIC ACIDS AND DALAPON IN DRINKING WATER BY LIQUID-LIQUID EXTRACTION, DERIVATIZATION AND GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION.

1.0 Scope and Application

0.1 This is a gas chromatographic (GC) method applicable to the determination of the listed haloacetic acids in drinking water, ground water, raw source water, and water at any intermediate treatment stage. In addition, the chlorinated herbicide, Dalapon, may be determined using this method. This method should be used by, or under supervision of experienced analysts. The analysts should be skilled in liquid-liquid extractions, derivatization procedures, and the use of GC and interpretation of gas chromatograms. This method is for use in the Environmental Protection Agency's (EPA's) data gathering and monitoring programs under the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensations, and Liability Act, and the Safe Drinking Water Act.

0.2 Target compounds (CAS #) that can be measured using this SOP include the following:

Bromochloroacetic Acid (BCA)	5589-96-3
Bromodichloroacetic Acid (BDCA)	7113-314-7
Chlorodibromoacetic Acid (CDBA)	5278-95-5
Dalapon	75-99-0
Dibromoacetic Acid (DBA)	631-64-1
Dichloroacetic Acid (DCA)	79-43-6
Monobromoacetic Acid (MBA)	79-08-3
Monochloroacetic Acid (MCA)	79-11-8
Tribromoacetic Acid (TBA)	75-96-7
Trichloroacetic Acid (TCA)	76-03-9

0.3 This method is applicable to the determination of the target analytes over the concentration ranges typically found in drinking water. Experimentally determined method detection limits (MDLs) for the above listed analyses are provided in Table 2. Actual MDLs may vary according to the particular matrix analyzed and the specific instrumentation employed. The haloacetic acids are observed ubiquitously in chlorinated drinking water supplies at concentrations ranging from <1 to >50 μg/L.

0.4 The following compounds may require special attention when being determined by this method:

0.4.1 Methylation using acidic methanol results in a partial decarboxylation of tribromoacetic acid. Therefore a substantial peak for bromoform will be observed in the chromatograms. Its elution does not, however, interfere with any other analytes. This demonstrates the

need for procedural standards to establish the calibration curve by which unknown samples are quantitated.

0.4.2 BCA co-eludes with an interferent on a DB-1701 column. However, because of the difference in peak shapes, the peak for the BCA tends to "ride on" the interferent peak and quantitative confirmation can be performed by manual integration that includes only the peak area of BCA.

0.5 Each analyst that uses this method must demonstrate the ability to generate acceptable results using the procedure in section 9.2.

0.6 When this method is used for the analyses of waters from unfamiliar sources, it is strongly recommended that analyte identifications be confirmed by GC using a dissimilar column or by GC/MS if concentrations are sufficient.

1 Summary of Method

1.1 40-mL aqueous samples at specified pH are extracted with methyl-tert-butyl-ether (MTBE). The haloacetic acids that have been partitioned into the organic phase are then converted to their methyl esters by derivatization procedures. Derivatization involves the addition of acidic methanol followed by slight heating. The acidic extract is neutralized by a back extraction with a saturated solution of sodium bicarbonate.

1.2 Target analytes are identified and measured by capillary column gas chromatography using an electron capture detector (GC/ECD). Analytes are quantitated using procedural standard calibration. Calculations are based on equations from procedural standards and associated calibration curves injected at the same time.

1.3 Instrumental and volume variances are corrected using internal standardization.

2 Definitions

The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible.

2.1 GC/MS - gas chromatography/mass spectrometry

2.2 Reagent water - Reagent water is defined as a water in which an interference is not observed $\geq$ to the MDL of each analyte of interest. A Millipore or Barnstead water system or its equivalent may be used to generate deionized reagent water. Distilled water that has been passed through granular charcoal may also be suitable. Reagent water is monitored through analysis of the laboratory reagent blank.

2.3 Quality control sample (QCS) - A solution of method analytes of known concentration which is used to fortify an aliquot of reagent water or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

2.4 Laboratory fortified blank (LFB)- A reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

2.5 Laboratory reagent blank (LRB)- A reagent water sample that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

2.6 Laboratory fortified matrix (LFM)- An environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

2.7 Laboratory duplicate - Two aliquots LD1 and LD2 of the same sample designated as such in the laboratory. Each aliquot is extracted, derivatized and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

2.8 Target compound - An analyte or compound listed in section 1.2.

2.9 Surrogate standards (SA)- A pure analyte(s) that is chemically similar to the target compounds but is not expected to occur in an environmental sample. It is added to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

2.10 Internal standard (IS)- A pure analyte(s) that is not a sample component but rather a closely related compound whose presence in environmental samples is highly unlikely. It is added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution.

2.11 Stock standard solution (SSS) - A concentrated solution containing one or more method analytes

prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

2.12 Primary dilution standard solution (PDS) - A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

2.13 Calibration standard (CAL) - A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

2.14 Continuing calibration check (CCC) -- A calibration standard containing one or more method analytes which is analyzed periodically to verify the accuracy of the existing calibration curves or response factors for those analytes.

2.15 Relative Response Factor (RRF) - Defined by the equation:

$$RRF = \frac{A_a \text{ x } C_{is}}{A_{is} \text{ x } C_a}$$

Where:

A_a = Peak area (or height) of the target or surrogate compound.
A_{is} = Peak area (or height) of the internal standard.
C_a = Concentration of the target or surrogate compound, in ,μg/L.
C_{is} = Concentration of the internal standard, in μg/L.

2.16 Laboratory performance check solution (LPC) - A solution of selected method analytes used to evaluate the performance of the instrumental system with respect to a defined set of method criteria.

2.17 Method detection limit (MDL) - The (MDL) is defined as the minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the concentration is greater than zero.

2.18 Estimated detection limit (EDL) - Defined as either the MDL or a level of a compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately 5, whichever is greater.

2.19 Procedural standard calibration - A calibration method where aqueous calibration standards are prepared and processed (e.g. purged, extracted and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

2.20 Material safety data sheet (MSDS) - Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire and reactivity data including storage, spill, and handling precautions.

3 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks as described in Section 9.4 Subtracting blank values from sample results is not permitted.

3.2 The use of high purity reagents and solvents helps to minimize interference problems. Each new bottle of solvent should be analyzed before use. An interference free solvent is a solvent containing no peaks yielding data at ≥ MDL (Table 2) and at the retention times of the analytes of interest. Purification of solvents by distillation in an all glass system may be required.

3.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the water sampled. Analyte identifications should be confirmed using the confirmation column specified in Table 1 (DB-17, RTX-35, RTX-50) or by GC/MS if the concentrations are sufficient.

3.4 Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. Solvent injections should be run after samples suspected of being highly concentrated to prevent carryover.

3.5 Column bleed may also cause interferences, especially at the elevated temperatures required if higher-boiling oils are present in the sample. Low-bleed GC columns and septa designed for high-temperature application are available.

3.6 Analytical bias may result from discrimination at the GC inlet. This can be minimized by optimizing the inlet configuration and injection technique.

4 Safety

The toxicity or carcinogenicity of each target compound or reagent has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses. The toxicity of the extraction solvent, MTBE, has not been well defined.

Susceptible individuals may experience adverse affects upon skin contact or inhalation of vapors. Therefore protective clothing and gloves should be used and MTBE should be used only in a chemical fume hood or glove box. The same precaution applies to pure standard materials.

5 Equipment and Supplies

Note: Brand names, suppliers, and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory

5.1 Glassware -- Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap water and reagent water. Drain and allow to dry. Thoroughly rinse with reagent grade acetone and hexane. After drying and cooling, store glassware in a clean environment free of all potential contamination. To prevent any accumulation of dust or other contaminants, store glassware inverted or capped with aluminum foil.

5.1.1 125 ml amber glass bottles with Teflon-lined screw cap (sample collection)

5.1.2 60 ml clear glass vials with Teflon-lined screw caps for sample extraction.

5.1.3 15-ml Hach tubes with Teflon-lined screw caps for derivatization process, one per sample.

5.1.4 Disposable glass Pasteur pipette

5.1.5 Micro syringes or Eppendorf pipette and tips.

5.1.6 Hewlett Packard autosampler vials

5.1.7 100 ml, 10 ml and 5 ml volumetric flasks with stoppers

5.1.8 Amber glass vials (1-10 ml) with Teflon lined-screw caps for standard storage.

5.2 Hydrogen carrier gas 99.9999+% grade (provided by a Balston Hydrogen generator)

5.3 Nitrogen make-up detector gas 99.9999+ grade (provided by a Peak nitrogen generator)

5.4 Millipore or Barnstead water polishing system capable of producing type I water. (See manual)

5.5 Analytical balance capable of weighing to 0.01 g.

5.6 Block heater, or sand bath, or Zymarck capable of holding Hach tubes.

5.7 Hewlett Packard 5890 Gas Chromatograph with data system

5.7.1 The GC must be capable of temperature programming and be equipped with a splitless injector.

5.7.2 GC supplies including injection port liners, ferrules, syringes etc...

5.7.3 The gas chromatograph must be equipped with an electron capture detector.

5.7.4 An autoinjector is recommended for improved precision of analytes.

5.7.5 The interfaced data system is the LabSystems XChrom/Atlas or an equivalent system which allows for data acquisition, storage, and retrieval. (See the manual for details)

5.7.6 Capillary column 30 meters long, 0.25mm ID, 0.25 micron film thickness or equivalent.

5.7.7 Primary GC column Restek RTX-1701or equivalent column.

5.7.8 Confirmation GC column Restek RTX-35 or equivalent column.

6 Reagents and Standards

6.1 Reagent water

6.2 Solvents
Optima grade or nanograde or distilled in glass or in other words the highest purity to reduce any interference problems. The residue grade solvents are flammable and stored in appropriate flammable storage in the solvent vault located off the chemical storage room. Reagent grade inorganic chemicals shall be used in all tests.

6.2.1	Acetone	Optima or Nanograde
6.2.2	Methanol	Optima or Nanograde
6.2.3	Methyl t-butyl ether	Optima or Nanograde
6.2.4	Hexane	Optima or Nanograde

6.3 Reagents and solutions

6.3.1 Sulfuric acid (H_2SO_4)

6.3.2 10% H_2SO_4/Methanol solution - Use caution when preparing sulfuric acid solutions. To prepare a 10% solution, (add 5 ml sulfuric acid drop-wise (due to heat evolution)to 20-30 mL methanol contained in a 50.0 mL volumetric flask that has been placed in a cooling bath. Then dilute to the 50.0 ml mark with methanol.

6.3.3 Sodium sulfate (Na_2SO_4) - (ACS) granular, anhydrous. If interferences are observed, it may be necessary to heat the sodium sulfate in a shallow tray at 400°C for up to 4 hr. to remove phthalates and other interfering organic substances. Alternatively, it can be extracted with methylene chloride in a Soxhlet apparatus for 48 hr. Store in a capped glass bottle rather than a plastic container.

6.3.4 Saturated sodium bicarbonate solution - Add sodium bicarbonate to a volume of water, mixing periodically until the solution has reached saturation.

6.3.5 Copper II sulfate pentahydrate ($CuSO_4$-$5H_2O$) - ACS reagent grade.

6.3.6 Sodium bicarbonate ($NaHCO_3$) - ACS reagent grade.

6.3.7 Ammonium chloride (NH_4Cl) - ACS reagent grade, used to convert free chlorine to monochloroamine. Although this is not the traditional dechlorination mechanism, ammonium chloride is categorized as a dechlorinating agent in this method.

6.4 Reference standards -- Supplied by Supelco or equivalent. The stock standard solutions are stored in bottles with PTFE-lined screw-caps. Store, protected from light, at -10°C or less or as recommended by the standard manufacturer. All standards are stored in the freezer or refrigerator in the dishwasher room or Rm. 312. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.4.1 Internal standard - 1,2,3-Trichloropropane (Supelco #47669-U @ 1000ug/mL). From this stock standard solution, prepare a primary dilution standard in MTBE at a concentration of 25 μg/ml by diluting 125 μl to 5 mL. Spike 25 μL where applicable for a final concentration of 0.625 ng/μL.

6.4.2 Surrogate standard - 2-Bromopropanoic Acid (Chemservice F2444S @ 2000μg/mL). From this stock standard solution, prepare a primary dilution standard in MTBE at a concentration of 20 μg/ml by diluting 50 μl to5 ml. Spike 10 μl where applicable for a final concentration of 5 ug/mL.

6.4.3 Laboratory performance check standards - Individual and mixed ester and acetate standards used to evaluate the performance of the instrumental system and retention times with respect to a defined set of method criteria.

6.4.4 Primary dilution standards (PDS) - Standard Spike - Prepare the primary dilution standard solution by combining and diluting stock standard solutions with MTBE. This primary dilution standard solution can be stored at 4ºC and protected from light. It is stable for at least one month but should be checked before use for signs of evaporation. See table 4 for a list of concentrations the can be used for the standard spike.

NOTE: When purchasing commercially prepared standards, solutions prepared in methanol must not be used because it has been found that the haloacetic acids are subject to spontaneous methylation when stored in this solvent. Furthermore, tribromoacetic acid has been found to be unstable in methanol because it undergoes decarboxylation when stored in this solvent.

6.4.5 Calibration standards (Procedural standards) - Calibration is performed by extracting procedural standards, i.e.; fortified reagent water, by the procedure set forth in Section 11. The desired amount of each MTBE calibration standard is added to separate 100 ml aliquots of reagent water to produce a calibration curve ranging from the detection limit to approximately 50 times the detection limit. Also, the reagent water used for the procedural standards contains ammonium chloride at the same concentration as that in the samples as per Section 11. See table 4 for a list of analyte concentrations.

7 Sample collection, preservation, storage, and hold time

7.1 Sample vial preparation

7.1.1 Grab samples must be collected in accordance with conventional sampling practices using amber glass containers with Teflon lined screw-caps and capacities of 125 ml.

7.1.2 Prior to shipment to the field, 12 mg crystalline or granular ammonium chloride (NH_4Cl) is added to the sample container. (For a concentration of 100 mg/L in the sample)

NOTE: Enough ammonium chloride must be added to the sample to convert the free chlorine residual in the sample matrix to combined chlorine. Typically, the ammonium chloride concentration here will accomplish that. If high doses of chlorine are used, additional ammonium chloride may be required.

7.2 Sample collection

7.2.1 Fill sample bottles to just overflowing but take care not to flush out the ammonium

chloride.

7.2.2 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 3-5 minutes). Remove the aerator so that no air bubbles can be visibly detected and collect samples from the flowing system.

7.2.3 When sampling from an open body of water, fill a 1-quart wide-mouth bottle or 1-liter beaker with sample from a representative area, and carefully fill sample vials from the container.

7.2.4 After collecting the sample in the bottle containing the ammonium chloride, seal the bottle and agitate by hand for 1 min.

7.3 Sample storage and hold times

7.3.1 Samples must be iced or refrigerated at 4°C and maintained at these conditions away from light until extraction. Synthetic ice (i.e., blue ice) is not recommended. Holding studies performed to date have suggested that, in samples preserved with NH_4Cl, the analytes are stable for up to 14 days. Since stability may be matrix dependent, the analyst should verify that the prescribed preservation technique is suitable for the samples under study.

7.3.2 Extracts (11.2.9) must be stored at 4°C or less away from light in glass vials with Teflon-lined caps. Extracts must be analyzed within 7 days from extraction if stored at 4°C or within 14 days if stored at -10°C or less.

8 Quality Control

Each laboratory that uses this method is required to operate a formal quality control (QC) program. Minimum quality control requirements are monitoring the laboratory performance check standard, initial demonstration of laboratory capability, performance of the method detection limit study, analysis of laboratory reagent blanks and laboratory fortified sample matrices, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample, blank and CCC, and analysis of QC samples. Additional QC practices may be added.

8.1 Laboratory performance check standard (LPC)
At the beginning of an analysis set, prior to any calibration standard or sample analysis and after an initial solvent analysis, a laboratory performance check standard must be analyzed. This check standard insures proper performance of the GC by evaluation of the instrument parameters of detector sensitivity, peak symmetry, and peak resolution. It furthermore serves as a check on the continuity of the instrument's performance. In regards to sensitivity, it allows the analyst to ascertain that this parameter has not changed drastically since the analysis of the MDL study. Inability to demonstrate acceptable instrument performance indicates the need for re-evaluation of

the instrument system. Criteria are listed in Table 5.

If column or chromatographic performance cannot be met, one or more of the following remedial actions should be taken. Break off approximately 1 meter of the injector end of the column and re-install, install a new column, adjust column flows or modify the oven temperature program.

8.2 Initial demonstration of capability

8.2.1 Calibrate for each analyte of interest as specified in Section 10. Select a representative fortification concentration for each of the target analytes. Prepare 4-7 replicates laboratory fortified blanks by adding an appropriate aliquot of the primary dilution standard or quality control sample to reagent water. (This reagent water should contain ammonium chloride at the same concentration as that specified for samples as per Section 8.1.2.) Analyze the LFBs according to the method beginning in Section 11.

8.2.2 Calculate the mean percent recovery and the standard deviation of the recoveries. For each analyte, the mean recovery value, expressed as a percentage of the true value, must fall in the range of 80-120% and the relative standard deviation should be less than 20%. For those compounds that meet these criteria, performance is considered acceptable and sample analysis may begin. For those compounds that fail these criteria, this procedure must be repeated using 4-7 fresh samples until satisfactory performance has been demonstrated. Maintain these data on file to demonstrate initial capabilities.

8.2.3 Furthermore, before processing any samples, the analyst must analyze at least one laboratory reagent blank to demonstrate that all glassware and reagent interferences are under control.

8.2.4 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. As laboratory personnel gain experience with this method, the quality of data should improve beyond those required here.

8.2.5 The analyst is permitted to modify GC columns, GC conditions, internal standard or surrogate compounds. Each time such method modifications are made, the analyst must repeat the procedures in Section 9.2.1 through Section 9.2.4 and Sect. 9.3.

8.3 Method detection study

8.3.1 Prior to the analysis of any field samples, the method detection limits must be determined. Initially, estimate the concentration of an analyte which would yield a peak equal to 5 times the baseline noise and drift. Prepare seven replicate laboratory fortified blanks at this estimated concentration with reagent water that contains ammonium

chloride at the same concentration as that specified for samples as per Section 8.1.2. Analyze the LFB's according to the method beginning in Section 11.

8.3.2 Calculate the mean recovery and the standard deviation for each analyte. Multiply the student's t value at 99% confidence and n-1 degrees of freedom (3.143 for seven replicates) by this standard deviation to yield a statistical estimate of the detection limit. This calculated value is the MDL.

8.3.3 Since the statistical estimate is based on the precision of the analysis, an additional estimate of detection can be determined based upon the noise and drift of the baseline as well as precision. This estimate is the EDL (Table 2).

8.4 Laboratory reagent blanks (LRB) -- Each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If the LRB produces an interferent peak within the retention time window (Section 12.3) of any analyte that would prevent the determination of that analyte or a peak of concentration greater than the MDL for that analyte, the analyst must determine the source of contamination and eliminate the interference before processing samples. Field samples of an extraction set associated with an LRB that has failed the specified criteria are considered suspect.

NOTE: Reagent water containing ammonium chloride at the same concentrations as in the samples (Section 8.1.2) is used to prepare the LRB.

8.5 Laboratory fortified blank (LFB) -- Since this method utilizes procedural calibration standards, which are fortified reagent water, there is no difference between the LFB and the continuing calibration check standard. Consequently, the analysis of an LFB is not required (Section 10.2).

8.6 Laboratory fortified sample matrix (LFM)

8.6.1 Chlorinated water supplies will usually contain significant background concentrations of several method analytes, especially dichloroacetic acid (DCA) and trichloroacetic acid (TCA). The concentrations of these acids may be equal to or greater than the fortified concentrations. Relatively poor accuracy and precision may be anticipated when a large background must be subtracted. For many samples, the concentrations may be so high that fortification may lead to a final extract with instrumental responses exceeding the linear range of the electron capture detector. If this occurs, the extract must be diluted. In spite of these problems, sample sources should be fortified and analyzed as described below. By fortifying sample matrices and calculating analyte recoveries, any matrix induced analyte bias is evaluated.

8.6.2 The laboratory must add known concentrations of analytes to one sample per extraction set or a minimum of 10% of the samples, whichever is greater. The concentrations should

be equal to or greater than the background concentrations in the sample selected for fortification. If the fortification level is less than the background concentration, recoveries are not reported. Over time, samples from all routine sample sources should be fortified.

8.6.3 Calculate the mean percent recovery, R, of the concentration for each analyte, after correcting the total mean measured concentration, A, from the fortified sample for the background concentration, B, measured in the unfortified sample, i.e.:

$$R = 100 (A - B) / C$$

where C is the fortifying concentration. In order for the recoveries to be considered acceptable, they must fall between 70% and 130% for all the target analytes.

8.6.4 If a recovery falls outside of this acceptance range, a matrix induced bias can be assumed for the respective analyte and the data for that analyte must be reported to the data user as suspect due to matrix effects.

8.7 Assessing surrogate recovery

The surrogate analyte is fortified into the aqueous portion of all continuing calibration standards, samples and laboratory reagent blanks. The surrogate is a means of assessing method performance in every analysis from extraction to final chromatographic performance.

8.7.1 When surrogate recovery from a sample, blank or CCC is < 70% or > 130%, check (1) calculations to locate possible errors, (2) standard solutions for degradation, (3) contamination, and (4) instrument performance. If those steps do not reveal the cause of the problem, re-analyze the extract.

8.7.2 If the extract re-analysis meets the surrogate recovery criterion, report only data for the re-analyzed extract.

8.7.3 If the extract re-analysis fails the 70-130% recovery criterion, the analyst should check the calibration by analyzing the most recently acceptable continuing calibration check standard. If the CCC fails the criteria of Section 10.2, re-calibration is in order per Section 10.1. If the CCC is acceptable, it may be necessary to extract another aliquot of sample. If the sample re-extract also fails the recovery criterion, report all data for that sample as suspect.

8.8 Assessing the internal standard (IS)

8.8.1 The analyst must monitor the IS response (peak area or peak height) of all injections during each analysis day. A mean IS response should be determined from the five point calibration curve. The IS response for any run should not deviate from this mean IS response by more than 30%. It is also acceptable if the IS response of a injection is within 15% of the daily continuing calibration standard IS response.

8.8.2 If a deviation greater than this occurs with an individual extract, optimize instrument performance and inject a second aliquot of that extract.

8.8.3 If the re-injected aliquot produces an acceptable internal standard response, report results for that aliquot.

8.8.4 If a deviation of greater than 30% is obtained for the re-injected extract, the analyst should check the calibration by analyzing the most recently acceptable CCC. If the CCC fails the criteria of Section 10.2, re-calibration is in order per Section 10.1. If the CCC is acceptable, analysis of the sample should be repeated beginning with Section 11, provided the sample is still available. Otherwise, report results obtained from the re-injected extract, but annotate as suspect.

8.9 Quality control sample (QCS) -- At least quarterly, analyze a QCS from an external source. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

8.10 The laboratory may adapt additional QC practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

9 Calibration and standardization

9.1 Initial calibration curve

9.1.1 Calibration is performed by extracting procedural standards by the procedure set forth in Section 11. A 5-8 point calibration curve is to be prepared by diluting the primary dilution standard into MTBE at the appropriate levels. The desired amount of each MTBE calibration standard is added to separate 100 mL aliquots of reagent water to produce a calibration curve ranging from the detection limit to approximately 50 times the detection limit. Also, the reagent water used for the procedural standards contains ammonium chloride at the same concentration as that in the samples as per Section 8.1.2.

9.1.2 Establish GC operating parameters equivalent to the suggested specifications in Table 1. The GC system must be calibrated using the internal standard (IS) technique. Other columns or conditions may be used if equivalent or better performance can be demonstrated.

9.1.3 A minimum of five calibration standards are required. The lowest should contain the

analytes at a concentration near to but greater than the MDL (Table 2) for each compound. The others should be evenly distributed throughout the concentration range expected in the samples.

9.1.4 Inject 2 μL of each calibration standard extract and tabulate peak height or area response and concentration for each analyte and the internal standard.

9.1.5 Generate a calibration curve by plotting the area ratios (A_a/A_{is}) against the concentration C_a of the calibration standards where A_a is the peak area of the analyte. A_{is} is the peak area of the internal standard. C_a is the concentration of the analyte. This curve can be defined as either first or second order. Also, the working calibration curve must be verified daily by measurement of one or more calibration standards (Section 10.2). If the response for any analyte falls outside the predicted response by more than 30%, the calibration check must be repeated using a freshly prepared calibration standard. Should the retest fail, a new calibration curve must be generated.

9.1.6 Alternately, an average relative response factor can be calculated and used for quantitation. Relative response factors are calculated for each analyte at the concentration levels using the equation below:

$$RRF = \frac{A_a \text{ x } C_{is}}{A_{is} \text{ x } C_a}$$

Where:
A_a = Peak area of the target or surrogate compound.
A_{is} = Peak area (or height) of the internal standard.
C_a = Concentration of the target or surrogate compound.
C_{is} = Concentration of the internal standard, in µg/L.

If the RRF value over the working range is constant (<20% RSD), the RRF can be assumed to be invariant and the average RRF used for calculations. Also, the average RRF must be verified daily by measurement of one or more calibration standards (Section 10.2). If the RRF for the continuing calibration standard deviates from the average RRF by more than 30%, the calibration check must be repeated using a freshly prepared calibration standard. Should the retest fail, a new calibration curve must be generated.

9.1.7 XChrom or Atlas may be used to collect the chromatographic data, calculate relative response factors, or calculate linear or second order calibration curves.

9.2 Continuing calibration check (CCC)

9.2.1 At least one CCC or LFB must be extracted with each set of samples. A CCC must be analyzed at the beginning of each analysis set, after every tenth sample analysis and after

the final sample analysis, to ensure that the instrument is still within calibration. These checks should be at two different concentration levels. Calculate analyte recoveries for all target analyses. In order for the calibration check to be considered valid and subsequently for the preceding ten samples to be considered acceptable with respect to calibration, recoveries must fall between 70% and 130% for all the target analyses.

NOTE: Continuing calibration check standards need not necessarily be different extracts but can be injections from the same extract as long as the holding time requirements (Sect. 8.3.2) are met.

9.2.2 If this criteria cannot be met, the continuing calibration check standard extract is re-injected in order to determine if the response deviations observed from the initial analysis are repeated. If this criteria still cannot be met, a second CCC should be extracted and analyzed or a CCC that has already been analyzed and has been found to be acceptable should be run. If this second CCC fails, then the instrument is considered out of calibration and needs to be re-calibrated.

10 Procedure

10.1 Sample extraction

10.1.1 Remove the samples from storage (Sect. 8.3.1) and allow them to equilibrate to room temperature.

10.1.2 Place 40 mL (40g $\pm$ 0.5g) of the water sample into a pre-cleaned 60 mL glass vial with a Teflon-lined screw cap.

10.1.3 Add 10μL of surrogate standard. (Section 7.4.2)

NOTE: When fortifying an aqueous sample with either surrogate or target analyses contained in MTBE, be sure that the needle of the syringe is well below the level of the water. After injection, cap the sample and invert once. This insures that the standard solution is mixed well with the water.

10.1.4 Adjust the pH to less than 0.5 by adding at least 2 mL of concentrated sulfuric acid. Cap, shake and then check the pH with a pH meter or narrow range pH paper.

10.1.5 Quickly add approximately 2 grams of copper II sulfate pentahydrate and shake until dissolved. This colors the aqueous phase blue and therefore allows for the analyst to better distinguish between the aqueous phase and the organic phase in this micro extraction.

10.1.6 Quickly add 16 grams of muffled sodium sulfate and shake for 3 to 5 minutes until almost all is dissolved. Sodium sulfate is added to increase the ionic strength of the aqueous phase and thus further drive the haloacetic acids into the organic phase. The addition of

this salt and the copper II sulfate should be done quickly so that the heat generated from the addition of the acid (Section 11.1.4) will help dissolve the salts.

10.1.7 Add 4.0 ml MTBE and place on the mechanical shaker for 30 minutes. (If hand-shaken, two minutes is sufficient if performed vigorously).

10.1.8 Allow the phases to separate for approximately 5 minutes.

10.2 Methylation

10.2.1 Using a disposable Pasteur pipette, transfer approximately 3 mL of the upper MTBE layer to a Hatch milk tube.

10.2.2 Add 1 ml 10% sulfuric acid in methanol to each tube.

10.2.3 Cap the tubes and place in the heating block at 50°C and maintain for 2 hr. The vials must fit snugly into the heating block to ensure proper heat transfer. At this stage, methylation of the method analyses is attained.

10.2.4 Remove the centrifuge tubes from the heating block and allow them to cool before removing the caps.

10.2.5 Add 4 ml saturated sodium bicarbonate solution to each centrifuge tube in 1 ml increments. Exercise caution when adding the solution because the evolution of CO_2 in this neutralization reaction is rather rapid.

10.2.6 Shake each centrifuge tube for 2 minutes. As the neutralization reaction moves to completion, it is important to continue to exercise caution by venting frequently to release the evolved CO_2.

10.2.7 Quantitatively transfer exactly 1.0 ml of the upper MTBE layer to an autosampler vial. A duplicate vial should be filled using the excess extract.

10.2.8 Add 25μL of internal standard (section 7.4.1) to the vial to be analyzed.

10.2.9 Analyze the samples as soon as possible. The sample extract may be stored up to 7 days if kept at 4°C or less or up to 14 days if kept at -10°C or less. Keep the extracts away from light in amber glass vials with Teflon-lined caps.

10.3 Gas chromatography

10.3.1 Table 1 summarizes recommended GC operating conditions and retention times observed

using this method. Other GC columns or chromatographic conditions may be used if the requirements of Section 9 are met.

10.3.2 Calibrate the system (Section 10.1) or verify the existing calibration by analysis of a CCC daily as described in Section 10.2.

10.3.3 Inject 2µl of the sample extract. Record the resulting peak sizes in area or height units.

10.3.4 If the response for the peak exceeds the working range of the system, dilute the extract, add an appropriate additional amount of internal standard and re-analyze. The analyst must not extrapolate beyond the calibration range established.

11 Data analysis and calculations

11.1 Identify sample components by comparison of retention times to retention data from the calibration standard analysis. If the retention time of an unknown peak corresponds, within limits (Section 12.3), to the retention time of a standard compound, then the identification is considered positive. Calculate analyte concentrations in the samples and reagent blanks from the calibration curves generated in Section 10.1.

11.2 If an average relative response factor has been calculated (Sect 10.1.6), analyte concentrations in the samples and reagent blanks are calculated using the following equation:

$$C_a = \frac{A_a \times C_{is}}{A_{is} \times RRF}$$

Where:
A_a = Peak area of the target or surrogate compound.
A_{is} = Peak area (or height) of the internal standard.
C_a = Concentration of the target or surrogate compound.
C_{is} = Concentration of the internal standard, in µg/L.

11.3 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatogram.

12 Method performance

12.1 The MDL data is given in Table 2. In addition, recovery and precision data were obtained at a

medium concentration for dechlorinated tap water (Table 3).

13 Pollution prevention

13.1 This method utilizes a micro-extraction procedure which requires the use of very small quantities of organic solvents. This feature reduces the hazards involved with the use of large volumes of potentially harmful organic solvents needed for conventional liquid/liquid extractions. This method also uses acidic methanol as the derivatizing reagent.

13.2 For information about pollution prevention that may be applicable to laboratory operations consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, D.C. 20036.

14 Waste management

14.1 Due to the nature of this method there is little need for waste management. No large volumes of solvents or hazardous chemicals are used. The matrices of concern are finished drinking water or source water. However, the Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel" also available from the American Chemical Society.

15 References

15.1 EPA method 552.2, revision 1.0, J.W. Hodgeson, J. Collins, R.E. Barth, D. Becker, D.J. Munch, J.W. Munch, A.M. Pawlecki
15.2 Quimby, B.D., Delaney, M.F., Uden. P.C. and Barnes, R.M. Anal. Chem. 52, 1980, pp. 259-263.
15.3 Uden, P.C. and Miller, J.W., J. Am. Water Works Assoc. 75, 1983, pp. 524-527.
15.4 Hodgeson, J.W. and Cohen, A.L. and Collins, J.D., "Analytical Methods for Measuring Organic Chlorination Byproducts", Proceedings Water Quality Technology Conference (WQTC-16), St. Louis, MO, Nov. 13-17, 1988, American Water Works Association, Denver, CO, pp. 981-1001.
15.5 Fair. P.S., Barth, R.C., "Comparison of the Microextraction Procedure and Method 552 for the Analysis of HAAs and Chlorophenols", Journal AWWA, November, 1992, pp. 94-98.
15.6 Chinn, R. and Krasner, S. " A Simplified Technique for the Measurement of Halogenated Organic Acids in Drinking Water by Electron Capture Gas Chromatography". Presented at the 28th Pacific Conference on Chemistry and Spectroscopy, Pasadena, CA, October, 1989
15.7 Hodgeson, J. W., Collins, J. D., and Becker, D. A., "Advanced Techniques for the Measurement of Acidic Herbicides and Disinfection Byproducts in Aqueous Samples," Proceedings of the 14th

Annual EPA Conference on Analysis of Pollutants in the Environment, Norfolk, VA., May 8-9, 1991. Office of Water Publication No. 821-R-92-001, U.S. Environmental Protection Agency, Washington, DC, pp 165-194.

15.8 Shorney, Holly L. and Randtke, Stephen J., "Improved Methods for Haloacetic Acid Analysis", Proceedings Water Quality Technology Conference, San Francisco, CA, November 6-10, 1994, American Water Works Association, pp 453-475.

15.9 Peters, Rund J.B., Erkelens, Corrie, De Leer, Ed W.B. and De Galan, Leo, "The Analysis of Halogenated Acetic Acids in Dutch Drinking Water", Wat. Res., Vol.25, No.4, 1991, Great Britain, pp 473-477.

15.10 "Carcinogens-Working with Carcinogens", Publication No. 77-206, Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute of Occupational Safety and Health, Atlanta, Georgia, August 1977.

15.11 "OSHA Safety and Health Standards, General Industry", (29CFR1910),OSHA 2206, Occupational Safety and Health Administration, Washington, D.C. Revised January 1976.

15.12 "Safety In Academic Chemistry Laboratories", 3rd Edition, American Chemical Society Publication, Committee on Chemical Safety, Washington, D.C., 1979.

15.13 Xie, Yuefeng, Reckhow, David A., and Rajan, R.V., "Spontaneous Methylation of Haloacetic Acids in Methanolic Stock Solutions", Environ. Sci. Technol., Vol.27, No.6, 1993, ppl232-1234.

15.14 ASTM Annual Book of Standards, Part 31, D3370, "Standard Practice for Sampling Water", American Society for Testing and Materials, Philadelphia, PA, p. 76, 1980.

15.15 ASTM Annual Book of Standards, Part 31, D3694, "Standard Practice for Preparation of Sample Containers and for Preservation", American Society for Testing and Materials, Philadelphia, PA, p. 679, 1980.

15.16 Glaser, J. A., Foerst, D. L., McKee, G. D., Quave, S. A. and Budde, W. L., Environ. Sci. Technol. I5, 1981, pp. 1426-1435.

17.0 Tables and Graphs

Table 1

Retention Data and Chromatographic Conditions

Analyte		Retention time, minutes	
		Column D_1	Column D_2
MCA	Monochloroacetic Acid	5.53	5.68
MBA	Monobromoacetic Acid	9.33	10.46
DCA	Dichloroacetic Acid	10.36	10.58
DAL	Dalapon	9.84	11.34
Surr	2-Bromopropanoic acid	10.81	12.15

IS	1,2,3-Trichloropropane	15.01	15.56
TCA	Trichloroacetic Acid	13.62	14.95
BCA	Bromochloroacetic Acid	15.39	16.18
DBA	Dibromoacetic Acid	19.13	20.71

Column D_1: Restek Rtx®-1701, 30 meter X 0.25 mm i.d., 0.25 μm film thickness
Injector temperature 225°C
Detector Temperature 300°C

Column E_2: Restek Rtx®-35, 30 meter X 0.25 mm i.d., 0.25 µm film thickness
Injector temperature 225°C
Detector Temperature 300°C
Splitless injection with a 45 second delay

Program: Hold at 35°C for 10 minutes,
Ramp to 70°C at 5°C/minute, no hold
Ramp to 100°C at 2°C/minute, no hold
Ramp to 250°C at 30°C/minute and hold for 10 minutes

Table 2

Analyte Accuracy and Precision Data and Method Detection Limits [a]

Level 1 in Reagent Water

Analyte	Fortified Conc. µg/L	Mean Meas Conc µg/L	Std Dev µg/L	Rel Std Dev µg/L %	Method detection limit [b] µg/L
MCA	0.90	1.21	0.25	20.5	0.78
MBA	0.60	0.61	0.09	14.3	0.27
DAL	0.60	0.69	0.16	23.4	0.51
DCA	0.90	1.41	0.44	31.3	1.39
2-Bromopropanoic acid	0.30	1.06	1.92	181.4	6.04
TCA	0.30	0.35	0.13	37.1	0.41
BCA	0.60	0.66	0.14	20.6	0.43
DBA	0.30	0.24	0.04	17.3	0.13

[a] Produced by analysis of seven aliquots of fortified reagent water.

[b] The method detection limit (MDL) is a statistical estimate of the detection limit. To determine the MDL for each analyte, the standard deviation of the mean concentration of the seven replicates is calculated. This standard deviation is then multiplied by the student's l-value at 99% confidence and n-1 degrees of freedom (3.143 for seven replicates). The result is the MDL.

Table 3:

Analyte Accuracy and Precision Data

Spiking Level (LFB) in reagent water[1]

Analyte	Fortified Concentration μg/L	Mean Measured Concentration μg/L	Standard Deviation μg/L	Relative Standard Deviation μg/L (%)
MCA	7.5	7.52	0.84	11.2
MBA	5.0	4.91	0.56	11.3
DAL	5.0	5.09	0.67	13.2
DCA	7.5	7.93	0.79	9.9
2-Bromopropanoic acid	5.0	5.22	0.53	10.1
TCA	2.5	2.27	0.22	9.8
BCA	5.0	4.60	0.49	10.6
DBA	2.5	2.08	0.28	13.7

Table 4:

[1]Data from seven aliquots of fortified reagent water

Standard Concentrations used currently in the Laboratory

Stock solution for Supelco #20238271, Standard spike (Std Spk) is diluted from stock solution 500μL into 10mL MTBE,
Calibration (working) standards are diluted and extracted from amounts listed into 200mL reagent water

Analyte	Stock Conc μg/mL	Std Spk Conc μg/mL	Std 1 μg/L (12μL)	Std 2 μg/L (20μL)	Std 3 μg/L (50μL)	Std 4 μg/L (200μL)	Std 5 μg/L (300μL)	Std 6 μg/L (500μL)
MCA	300	15	0.9	1.5	3.75	15.0	22.5	37.5
MBA	200	10	0.6	1.0	2.5	10.0	15.0	25.0
DAL	200	10	0.6	1.0	2.5	10.0	15.0	25.0
DCA	300	15	0.9	1.5	3.75	15.0	22.5	37.5
2-Bromopropanoic acid	100	5	0.3	0.5	1.25	5.0	7.5	12.5
TCA	100	5	0.3	0.5	1.25	5.0	7.5	12.5
BCA	200	10	0.6	1.0	2.5	10.0	15.0	25.0
DBA	100	5	0.3	0.5	1.25	5.0	7.5	12.5

Table 5

LABORATORY PERFORMANCE CHECK SOLUTION

PARAMETER	ANALYTE	CONC µg/mL in MTBE	ACCEPTANCE CRITERIA
INSTRUMENT SENSITIVITY	MCA	0.006	DETECTION OF ANALYTE S/N[a] > 3
CHROMATOGRAPHIC PERFORMANCE	BCA	0.004	PGF[b] BETWEEN 0.80 AND 1.15
COLUMN PERFORMANCE	CDBA	0.010	RESOLUTION[c] > 0.50
	SURROGATE (2,3-DBPA)	0.010	

[a]S/N is a ratio of peak signal to baseline noise.
peak signal - measured as height of peak.
baseline noise - measured as maximum deviation in baseline (in units of height) over a width equal to the width of the base of the peak.

[b]PGF = Peak Gaussian Factor

$$PGF = \frac{1.83 \times W_{1/2}}{W_{1/10}}$$

where: $W_{1/2}$ = the peak width at half height (in seconds).
$W_{1/10}$ = the peak width at one-tenth height (in seconds).

This is a measure of the symmetry of the peak.

[c]Resolution between two peaks is defined by the equation:

$$R = \frac{t}{W_{ave}}$$

where: t = the difference in elusion times between the two peaks.
W_{ave} = the average peak width of the two peaks (measurements taken at baseline).

This a measure of the degree of separation of two peaks under specific chromatographic conditions.